

## 에폭시 수지의 열 및 기계적 특성에 대한 Bridge Group의 영향

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## Influences of Bridge Group on Thermal and Mechanical Properties of Epoxy Resins

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**Abstract:** In order to obtain thermosetting epoxy resin, it is the prerequisite condition that the epoxy precursor must contain at least two epoxy groups. Thus, bridge group is needed to link the epoxy groups, and naturally, the chemical structure of the bridge group may also influence the thermomechanical performances of the cured epoxy resin. However, literature about the effects of bridge group on properties of cured epoxy is seldom published. To fill the gap, three model epoxy monomers containing different bridge groups have been synthesized from 4,4'-dihydroxydiphenyl, 1,1-bis(4-hydroxyphenyl)cyclohexane and bisphenol A in this work. After chemical structure confirmation, all of the monomers are cured by methylhexahydrophthalic anhydride (HMMPA), and the properties of the obtained cured network are evaluated by differential scanning calorimetry (DSC), dynamic thermomechanical analysis (DMA), tensile test and scanning electron microscope (SEM). The results show that bulky bridge group can effectively increase the glass transition temperature, enhance the tensile strength, and enlarge elongation at break of the cured epoxy resin.

**Keywords:** epoxy, bridge group, thermomechanical performance.

### Introduction

As one of excellent thermosetting materials, epoxy resin has been widely used in fields of coating,<sup>1,2</sup> adhesive,<sup>3</sup> electronic package,<sup>4</sup> 3D printing<sup>5</sup> and functional composite<sup>6</sup> due to its remarkable processability, prominent chemical and corrosion resistance, and wonderful thermal and mechanical properties.<sup>7</sup> However, the epoxy resins are facing more and more chal-

lenges in recent decades because the newly emerged applications request better thermal stability, higher mechanical performances, and so on.

To meet the new requirements, researchers have persistently directed toward improving the thermal and mechanical properties of epoxy resins. The most widely adopted method is adding rigid fillers into epoxy resins. Peng and coworkers uniformly dispersed rigid sulfonated polyamide in epoxy matrix, and the tensile strength of modified epoxy was increased by 1.2 fold than that of the neat epoxy.<sup>8</sup> Woo and coworkers used epoxidized soybean oil modified bisphenol A type epoxy resin to improve its toughness.<sup>9</sup> In addition to physical blending,

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researchers also justified that increasing the crosslinking densities is another efficient route to enhance the thermomechanical properties of epoxy resins as well. Schroeder *et al.* found the  $T_g$  values of the cured epoxy resins changed linearly with the crosslinking densities, furthermore, they also claimed that the tensile strength varied with crosslinking densities.<sup>10</sup> Since the epoxy thermosets are obtained by curing their processable and moldable precursors, and to obtain cured epoxy resins with admirable crosslinking densities, the precursors must contain at least two epoxy groups. Naturally, bridge group is needed to connect two or more epoxy groups, and thus, the nature of the bridge group also plays key role in determination of the thermomechanical performances of the cured epoxy resin. For this reason, deeply understanding the effect of the bridge group, especially the steric hindrance of the bridge group, on thermomechanical properties of epoxy resin becomes increasingly important and urgent, because it can provide a guide for design of the epoxy precursors which may demonstrate attractive thermomechanical properties after curing reaction. Some researchers had focused on the influences of bridge group on properties of epoxy resin, for example Lee and coworkers identified that ether bridge group endows the liquid crystalline epoxy with higher mechanical and thermal properties than the ester bridge group.<sup>11</sup> Moreover, they further proved that when the epoxy resins were bridged with long mesogenic groups, their storage modulus and glass transition temperature were can be effectively enhanced.<sup>12</sup> Unfortunately, they mainly concerned with the liquid crystalline epoxy,<sup>13</sup> and other researchers mainly focus on the influences of the bridge group in curing agent rather than in epoxy precursor itself.<sup>14</sup> Li *et al.* used oligomers to disclose valuable information about the effects of bridge group in epoxy on curing behaviors of epoxy resins,<sup>15</sup> however, instead of the pure monomers, they used oligomers which may cripple the relationships between the bridge group and properties of obtained epoxy resin because of the structure ambiguities of the oligomers. Thus, to deeply understand the influences of bridge group on thermomechanical properties of epoxy resin, the prerequisite matter is ruling

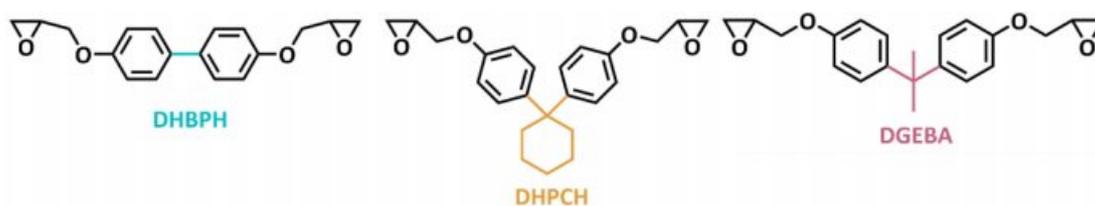
out the uncorrelated factors, and the most feasible approach is designing the model epoxy monomers. However, using the model epoxy monomers to inspect the influences of steric hindrance of the bridge group on curing behaviors of the monomer and the thermomechanical properties, to the best of our knowledge, there has no literature been published.

In this contribution, three model epoxy monomers (Scheme 1) with different volume of bridge groups, including carbon-carbon single bond,<sup>16,17</sup> cyclohexyl group and isopropyl bridge group<sup>18</sup> were synthesized again to investigate the effects, especially the steric hindrance, of bridge groups on thermomechanical properties of epoxy resins, and we hope that the results obtained in this study could shed light on the influences of bridge groups on performances of epoxy resins.

## Experimental

**Materials.** 4,4'-dihydroxydiphenyl (96%), 1,1-bis(4-hydroxyphenyl)cyclohexane (98%), bisphenol A (99%), methylhexahydrophthalic anhydride (HMMPA, 95%), tetrabutylammonium bromide (99%) and epichlorohydrin (99%) were purchased from Aladdin Chemical Reagent Co. (Shanghai, China). Sodium hydroxide (A.R. grade), chloroform (A.R. grade) and petroleum ether (A.R. grade) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All of reagents were used as received.

**Synthesis of 4,4'-bis(oxiran-2-ylmethoxy)-1,1'-biphenyl (DHBPH).** 18.6 g (100 mmol) of 4,4'-dihydroxydiphenyl, 148.0 g (1600 mmol) of epichlorohydrin and 0.93 g of tetrabutylammonium bromide were charged into a 500 mL round three-necked flask equipped with a nitrogen inlet, a condenser, a thermometer and a magnetic stirrer. After the reactor was stirred 2 h at 90 °C, the system was cooled down to room temperature, and the thermometer was replaced by a separatory funnel, 30.0 g (40 wt%) of aqueous sodium hydroxide solution were added into the reactor dropwise. The system was maintained at room temperature for another 24 h after the aqueous sodium hydroxide solution was completely added into the



**Scheme 1.** Chemical structure of three model epoxy monomers.

reactor. After that, the system was first diluted by around 300 mL of chloroform, and then washed by deionized water for several times to remove the excess sodium hydroxide. A fine white powder was obtained after being precipitated in petroleum ether and dried at 45 °C under vacuum (yield: 27%).

$^1\text{H}$  NMR (400 MHz, DMSO-*d*6)  $\delta$  7.59-7.50 (m, 4H), 7.08-6.97 (m, 4H), 4.35 (dd,  $J = 11.4, 2.6$  Hz, 2H), 3.86 (dd,  $J = 11.4, 6.6$  Hz, 2H), 3.36 (dd,  $J = 4.2, 2.6$  Hz, 2H), 2.85 (t,  $J = 4.7$  Hz, 2H), 2.72 (dd,  $J = 5.1, 2.6$  Hz, 2H).

$^{13}\text{C}$  NMR (101 MHz, DMSO-*d*6)  $\delta$  157.85, 133.01, 127.73, 115.37, 69.46, 50.20, 44.23.

FTIR (KBr),  $\text{cm}^{-1}$ : 3006  $\text{cm}^{-1}$  (benzene ring **C-H**), 2927  $\text{cm}^{-1}$  (oxirane ring **C-H**), 1240 and 811  $\text{cm}^{-1}$  (oxirane group **C-O-C**), 910  $\text{cm}^{-1}$  (oxirane ring).

Synthesis of 2,2'-(((cyclohexane-1,1-diylbis(4,1-phenylene)) bis(oxy)) bis(methylene)) bis(oxirane) (DHPCH). 26.8 g (100 mmol) of 1,1-bis(4-hydroxyphenyl)cyclohexane, 148.0 g (1600 mmol) of epichlorohydrin and 0.93 g of tetrabutylammonium bromide were charged into a 500 mL round three-necked flask equipped with a nitrogen inlet, a condenser, a thermometer and a magnetic stirrer. After the reactor was stirred 2 h at 90 °C, the system was cooled down to room temperature, and the thermometer was replaced by a separatory funnel, 30.0 g (40 wt%) of aqueous sodium hydroxide solution were added into the reactor dropwise. The system was maintained at room temperature for another 24 h after the aqueous sodium hydroxide solution was completely added into the reactor. After that, the system was first diluted by around 300 mL of chloroform, and then washed by deionized water for several times to remove the excess sodium hydroxide. Then, the mixture was separated into two layers in a separatory funnel, and the organic layer was collected and dried by anhydrous  $\text{MgSO}_4$ . A viscous and light yellow liquid was obtained after removing the solvent at 50 °C under vacuum (yield: 85%).

$^1\text{H}$  NMR (400 MHz, chloroform-*d*)  $\delta$  7.25 – 7.12 (m, 4H), 6.93 – 6.76 (m, 4H), 4.18 (dd,  $J = 11.0, 3.3$  Hz, 2H), 3.95 (dd,  $J = 11.0, 5.6$  Hz, 2H), 3.34 (dq,  $J = 7.4, 3.1$  Hz, 2H), 2.90 (t,  $J = 4.5$  Hz, 2H), 2.80 – 2.70 (m, 2H), 2.24 (t,  $J = 5.4$  Hz, 4H), 1.66 – 1.42 (m, 6H).

$^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  156.09, 141.57, 128.15, 114.22, 68.71, 50.19, 45.10, 44.77, 37.39, 26.42, 22.92.

FTIR (KBr),  $\text{cm}^{-1}$ : 3000  $\text{cm}^{-1}$  (benzene ring **C-H**), 2930 and 2856  $\text{cm}^{-1}$  (cyclohexyl and oxirane ring **C-H**), 1239 and 821  $\text{cm}^{-1}$  (oxirane group **C-O-C**), 912  $\text{cm}^{-1}$  (oxirane ring).

Synthesis of 2,2'-(((propane-2,2-diylbis(4,1-phenylene)) bis(oxy)) bis(methylene)) bis(oxirane) (DGEBA). 22.8 g (100 mmol) of bisphenol A, 148.0 g (1600 mmol) of epichlorohydrin and 0.93 g of tetrabutylammonium bromide were charged into a 500 mL round three-necked flask equipped with a nitrogen inlet, a condenser, a thermometer and a magnetic stirrer. After the reactor was stirred 2 h at 90 °C, the system was cooled down to room temperature, and the thermometer was replaced by a separatory funnel, 30.0 g (40 wt%) of aqueous sodium hydroxide solution were added into the reactor dropwise. The system was maintained at room temperature for another 24 h after the aqueous sodium hydroxide solution was completely added into the reactor. After that, the system was first diluted by around 300 mL of chloroform, and then washed by deionized water for several times to remove the excess sodium hydroxide. Then, the mixture was separated into two layers in a separatory funnel, and the organic layer was collected and dried by anhydrous  $\text{MgSO}_4$ . A viscous and transparent liquid was obtained after removing the solvent at 50 °C under vacuum (yield: 85%).

$^1\text{H}$  NMR (400 MHz, DMSO-*d*6)  $\delta$  7.26 – 7.00 (m, 4H), 6.94 – 6.75 (m, 4H), 4.26 (dd,  $J = 11.3, 2.7$  Hz, 2H), 3.80 (dd,  $J = 11.3, 6.5$  Hz, 2H), 3.30 (tt,  $J = 6.5, 2.7$  Hz, 2H), 2.91 – 2.76 (m, 2H), 2.69 (dd,  $J = 5.1, 2.6$  Hz, 2H), 1.58 (s, 6H).

$^{13}\text{C}$  NMR (101 MHz, DMSO-*d*6)  $\delta$  156.48, 143.37, 127.90, 114.33, 69.31, 50.21, 44.21, 41.63, 31.14.

FTIR (KBr),  $\text{cm}^{-1}$ : 3000  $\text{cm}^{-1}$  (benzene ring **C-H**), 2930 and 2856  $\text{cm}^{-1}$  (methyl and oxirane ring **C-H**), 1227 and 826  $\text{cm}^{-1}$  (oxirane group **C-O-C**), 913  $\text{cm}^{-1}$  (oxirane ring).

**Preparation of the Cured Epoxy Resins.** Each of the epoxy monomer was mixed with HMMPA at a fixed molar ratio of 1:1, and the mixture was dissolved in a small amount of chloroform or dimethyl sulfoxide at room temperature to get a light yellow liquid. Then the mixture was transferred to a steel mold and degassed for 30 min, followed by step-by-step heating at 120, 140, 160 and 180 °C for 2 h, respectively, and the obtained products were marked as DHBPH-HMMPA, DHPCH-HMMPA and DGEBA-HMMPA.

**Characterizations.** Nuclear magnetic resonance (NMR) spectra were performed on a Bruker AVANCE III 400 MHz at room temperature using chloroform-*d* or DMSO-*d*6 as the solvent. Fourier transform infrared (FTIR) spectra were obtained on a Thermo Scientific Nicolet iS30. Differential scanning calorimetry (DSC) was recorded on a NETZSCH DSC 214 under protection of high purity nitrogen gas, and the heating rate was 10 °C  $\text{min}^{-1}$ . Thermogravimetric analysis (TGA) was con-

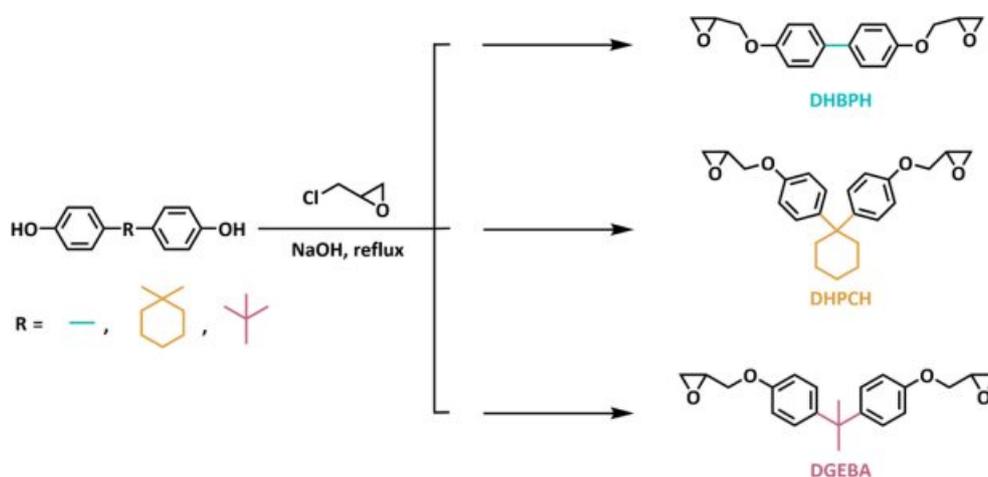
ducted on a Mettler-Toledo TGA/DSC1 thermogravimetric analyzer under pure nitrogen and pure air, and flow rate was fixed at  $50 \text{ mL min}^{-1}$ . Around 5 mg of cured epoxy sample was charged into an  $80 \mu\text{L}$  corundum crucible and heated from 50 to  $800 \text{ }^\circ\text{C}$  with a fixed heating rate of  $20 \text{ }^\circ\text{C min}^{-1}$ . Dynamic thermomechanical analysis (DMA) was performed on a TA Instruments Q800 under tensile mode with the amplitude of  $2 \mu\text{m}$ , and the data were collected from 0 to  $250 \text{ }^\circ\text{C}$  at rate of  $3 \text{ }^\circ\text{C min}^{-1}$ . Tensile tests were carried out on an Instron 5567 machine with a stretching rate of  $2 \text{ mm}\cdot\text{min}^{-1}$  at room temperature. The samples were prepared as rectangular shape, and the dimensions were  $25\times 5\times 2 \text{ mm}$  (length $\times$ width $\times$ thickness). For each sample, three specimens were tested, and the average value is taken as the tensile strength. The tensile sections of the samples were observed on a ZEISS EVO18 scanning electron microscope (SEM), and the sections of samples were sprayed gold for 12 min before testing.

## Results and Discussion

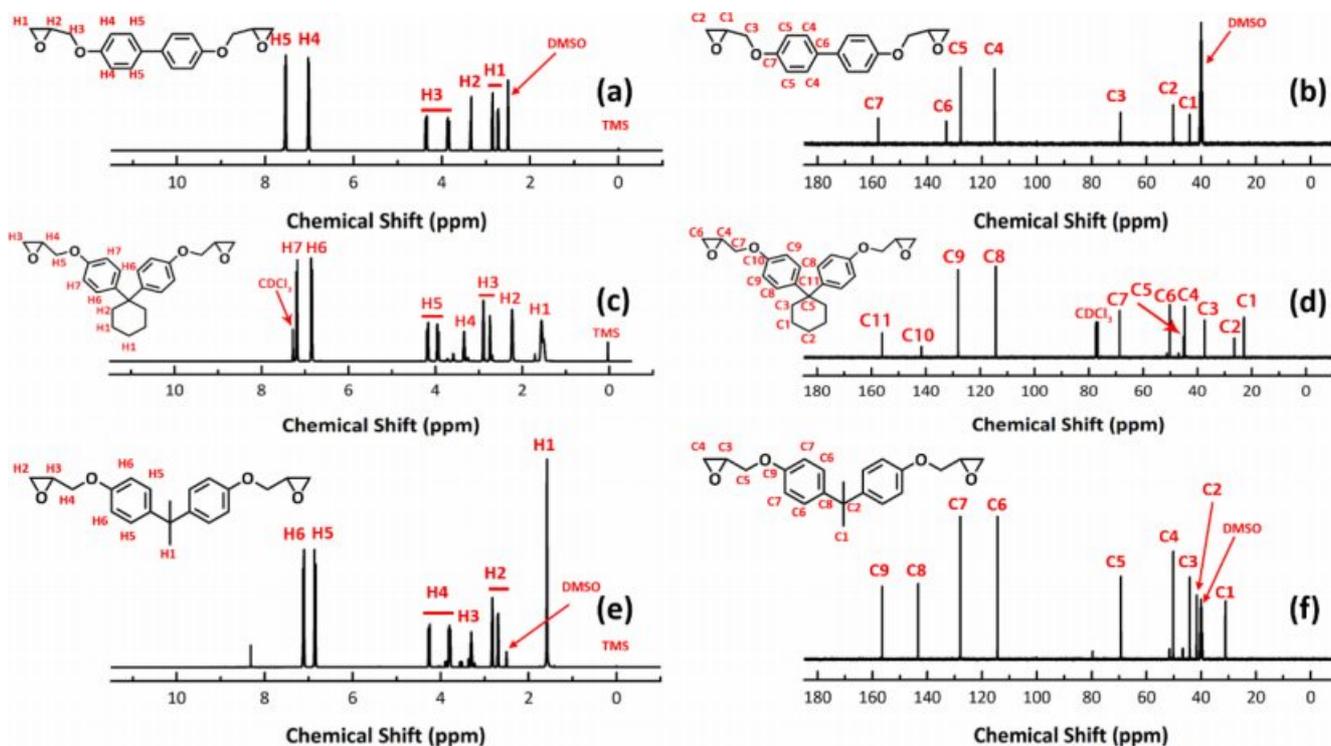
**Design, Synthesis and Characterization of DHPCH, DHBPH and DGEBA.** In this work, three model epoxy monomers were synthesized by a commonly reported route,<sup>19,20</sup> that is a general glycidylation reaction of phenolic hydroxyl with excess epichlorohydrin in the presence of sodium hydroxide and tetrabutylammonium bromide (Scheme 2). The chemical structure of obtained epoxy monomer is firstly characterized by means of  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR (Figure 1). Note that, depending on the solubility, NMR of DHPCH was recorded in chloroform-*d*, whereas the NMR spectra of DHBPH and DGEBA were obtained in DMSO-*d*<sub>6</sub>. In the  $^1\text{H}$

NMR, the three peaks at around 2.4, 2.6 and 3.2 ppm correspond to the three protons in oxirane groups (Figure 1(a), 1(c) and 1(e)).<sup>21</sup> The two peaks at about 6.7 and 7.2 ppm belong to the protons of benzene. Two additional peaks at 1.5 and 2.2 ppm (marked as H1 and H2) are attributed to the protons in cyclohexyl group of DHPCH (Figure 1(c)), and a large peak appears at 1.6 ppm (marked as H1) in Figure 1(e) is ascribed to protons in methyl group of DGEBA. The peaks appear at 4.3 and 4.8 ppm in Figure 1(a), 1(c) and 1(e) are attributed to the protons of  $-\text{CH}_2-$  groups. The  $^{13}\text{C}$  NMR spectra of DHBPH, DHPCH and DGEBA are exhibited in Figure 1(b), 1(d) and 1(f). As it is shown, the peaks at 43.5 and 50.1 ppm are attributed to the carbons in oxirane group, and signal at around 68.7 ppm corresponds to the carbons of  $-\text{CH}_2-$  group that connected to oxirane group.<sup>22</sup> Moreover, all other peaks are assigned to corresponding carbons accordingly.

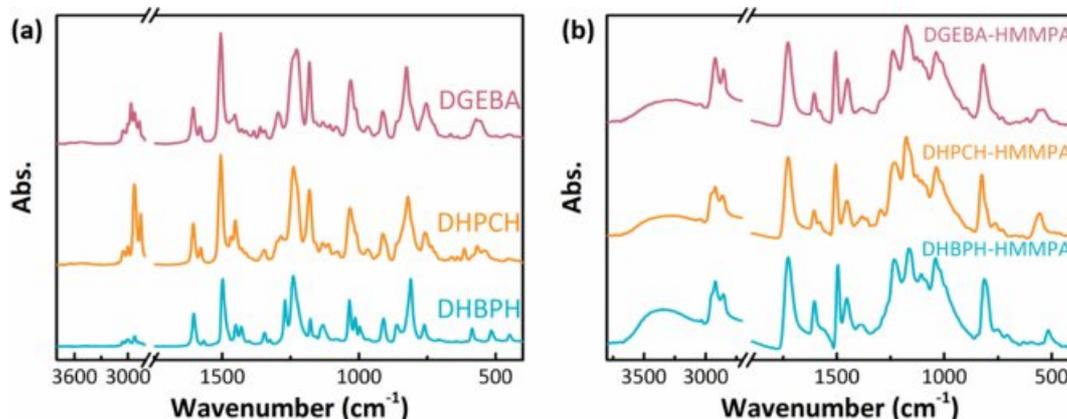
In addition to the NMR, the FTIR spectroscopy was also employed to further inspect the chemical structures both of monomers and cured resins (Figure 2). The characteristic peaks of the oxirane group has appeared at around  $1240$ ,  $910$  and  $810 \text{ cm}^{-1}$ , which correspond to the vibration of  $\text{C-O-C}$  ring.<sup>23,24</sup> The absorption bands display at  $1573 \text{ cm}^{-1}$  corresponds to the skeleton vibration in the benzene ring, and the signals at about  $1503 \text{ cm}^{-1}$  are ascribed to the C-H in plane bending vibration in the benzene ring (Figure 2(a)).<sup>25</sup> It is worth nothing that the bands correspond to asymmetric and symmetric stretching vibration of  $\text{C-H}$  display at about  $2970$  and  $2964 \text{ cm}^{-1}$ ,<sup>25</sup> and the two bands are more obvious in FTIR spectra of DHPCH and DGEBA than that of DHBPH. This is due to the presence of extra alkyl group in DHPCH (cyclohexyl group) and DGEBA (methyl group). After curing reac-



**Scheme 2.** Synthetic route for DHPCH, DHBPH and DGEBA.



**Figure 1.** NMR spectra of DHBPH, DHPCH and DGEBA: (a)  $^1\text{H}$  NMR of DHBPH; (b)  $^{13}\text{C}$  NMR of DHBPH; (c)  $^1\text{H}$  NMR of DHPCH; (d)  $^{13}\text{C}$  NMR of DHPCH; (e)  $^1\text{H}$  NMR of DGEBA; (f)  $^{13}\text{C}$  NMR of DGEBA.

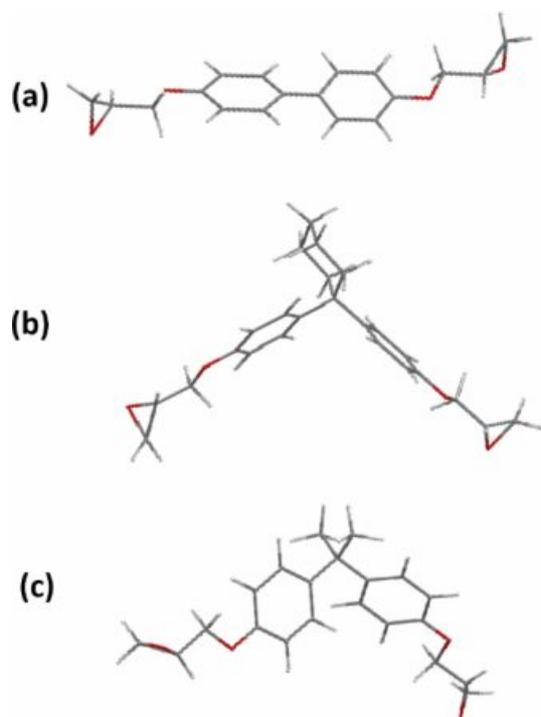


**Figure 2.** FTIR spectra of monomers and cured epoxy resins: (a) epoxy monomers; (b) cured epoxy resins.

tion, the characteristic bands of oxirane ring have disappeared in all FTIR spectra (Figure 2(b)), indicating the complete curing of epoxy monomers. Moreover, new signals appear at about  $1700\text{ cm}^{-1}$  are attributed the stretching vibration of  $\text{C}=\text{O}$  in curing agent. The broad bands centered at  $3300\text{ cm}^{-1}$  are due to the presence of hydroxyl groups which may further form hydrogen bonds in cured epoxy resins. With testing results of NMR and FTIR, it is concluded that the target epoxy monomers in high purity has been successfully synthesized and fully

cured by HMMPA.

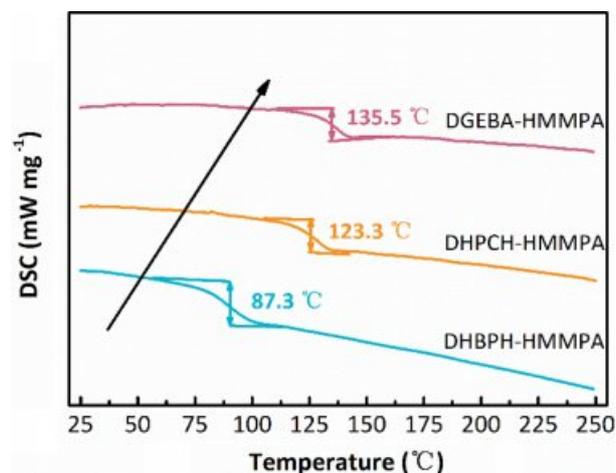
Moreover, the 3D chemical structures of DHBPH, DHPCH and DGEBA are presented in Figure 3. With the visual geometry of the three model epoxy monomers, it is easy to find that the DHBPH is the most stretched and linear one among the three model epoxy monomers, furthermore, the DHBPH almost shows almost no distortion, indicating that its bridge group ( $\text{C}-\text{C}$  single bond) does not bring any discernible steric hindrance to DHBPH. In contrast to the DHBPH, the other two



**Figure 3.** 3D chemical structures of the three model epoxy monomers.

epoxy monomers are twisted out of the molecular plane due to the presence of the different bridge groups (Figure 3). It should be noted that the DGEBA displays the most twisted configuration among them, due to the steric hindrance resulted from its bridge group.<sup>11</sup> Thus, it is easy to find that the bridge groups of the three model epoxy monomer can impose significantly varied steric hindrance on corresponding DHBPH, DHPCH and DGEBA, which can be further approved by testing the thermomechanical properties of corresponding cured epoxy resins.

**DSC Analysis of Different Cured Epoxy Resins.** In order to have a better understanding of the thermal performances of the cured resins, the thermal properties of DHBPH-HMMPA, DHPCH-HMMPA and DGEBA-HMMPA were monitored and assessed using a DSC and a TGA. For eval-



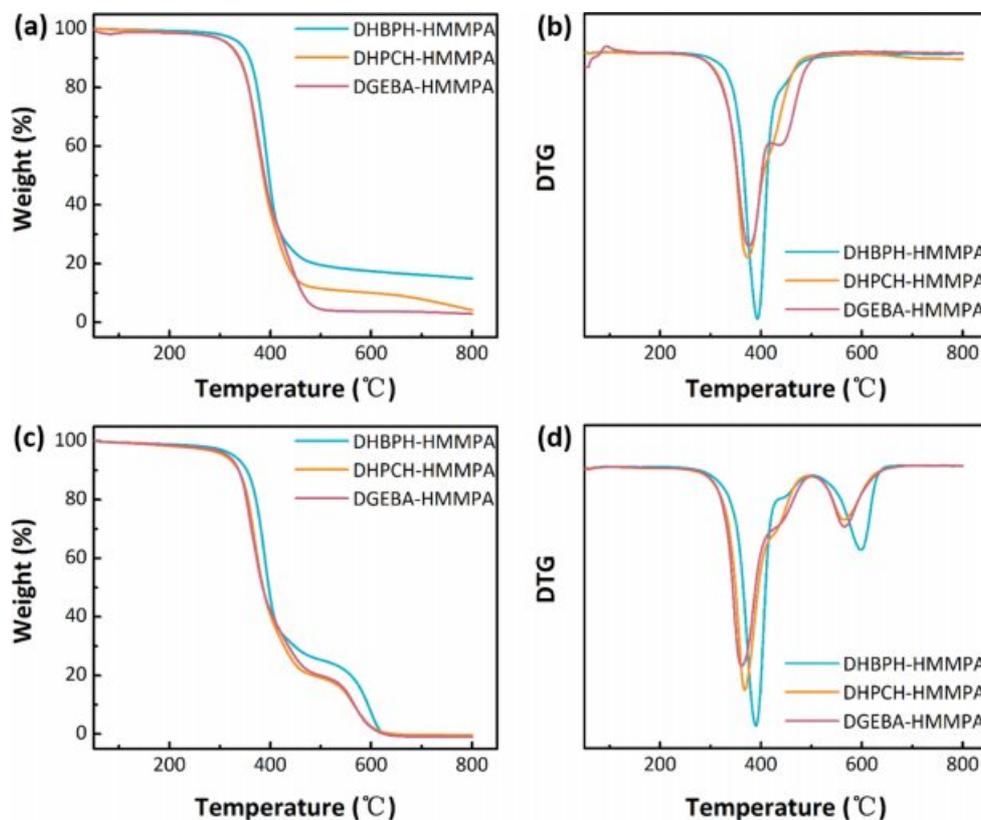
**Figure 4.** DSC thermogram of cured epoxy resin networks.

uation of the  $T_g$ , typical DSC curves of cured epoxy resins are obtained after eliminating the heat history and heating in a dynamic process at heating rate of  $10 \text{ K min}^{-1}$  under protection of high purity nitrogen gas (Figure 4).

Obviously, except for a parallel movement of the baseline toward the endothermic direction, neither exothermic peak nor endothermic peak has been observed in all DSC curves (Figure 4), suggesting the completeness of the curing reaction. Moreover, the  $T_g$  values are 87.3, 123.3 and 135.5 °C for DHBPH-HMMPA, DHPCH-HMMPA and DGEBA-HMMPA, respectively (Table 1). As it is shown, the DHBPH-HMMPA shows the lowest value of  $T_g$  (87.3 °C), and this is probably due to the biphenyl groups can rotate freely around the single bond. By contrast, the presence of the cyclohexyl group and isopropyl group in DHPCH and DGEBA lay significant steric hindrance on cured epoxy resins, which further severely restricts motion of the chain segments, and thus the  $T_g$  values of DHPCH-HMMPA and DGEBA-HMMPA are increased apparently. The phenomenon is also reported by other researchers, for example Balizer and coworkers used hindered and unhindered cure agent to cure DGEBA, and they found that using methyl group to substitute a hydrogen atom would apparently enhance the  $T_g$

**Table 1.** Parameters Obtained from the DSC and TGA Curves of DHBPH-HMMPA, DHPCH-HMMPA and DGEBA-HMMPA

Samples	$T_g$ from the DSC (°C)	$T_{d,5\%}$ (°C)		$T_{d,30\%}$ (°C)		$T_s$ (°C)		Char yield (% @ 800 °C)	
		Air	Nitrogen	Air	Nitrogen	Air	Nitrogen	Air	Nitrogen
DHBPH-HMMPA	91.8	309.7	339.7	421.3	448.3	184.6	198.4	0	14.9
DHPCH-HMMPA	126.0	315.7	315.7	413.3	427.3	183.4	187.5	0	4.2
DGEBA-HMMPA	137.3	328.1	328.1	420.1	436.0	187.8	192.5	0	2.9



**Figure 5.** TGA and DTG curves obtained both in nitrogen ((a) and (b)); in air ((c) and (d)) for DHBPH-HMMPA, DHPCH-HMMPA and DGEBA-HMMPA.

of cured epoxy resin, and Moreover, other research group also reported similar results.<sup>26,27</sup>

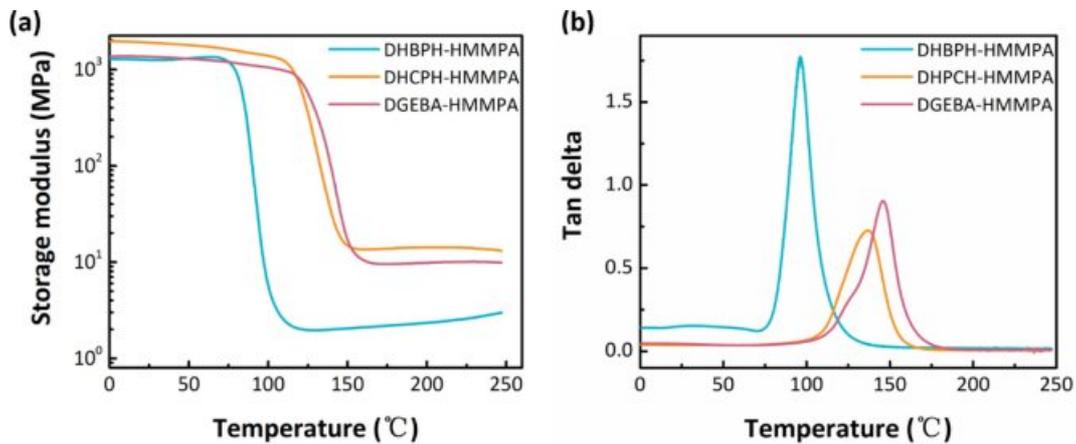
Thermal degradation processes of three cured epoxy resins both in air and nitrogen atmospheres were inspected by TGA (Figure 5). The  $T_{d,5\%}$  is taken as the characteristic temperature for evaluating the thermal stability of each cured epoxy resin, which has been listed in Table 1. Interestingly, although the DHBPH-HMMPA gives the highest  $T_{d,5\%}$  value, it seems that introduction of large bridge group can reduce the influences of the atmosphere on thermal stability of cured epoxy resin because compared with the DHBPH-HMMPA, the  $T_{d,5\%}$  values of DHPCH-HMMPA and DGEBA-HMMPA show no change both in air and nitrogen, whereas the  $T_{d,5\%}$  of DHBPH-HMMPA lower 30 °C when the atmosphere changes from nitrogen to air. Moreover, due to the high percent of aromatic groups in DHBPH-HMMPA, it demonstrates the highest percentage of char yield at 800 °C in nitrogen among three cured epoxy resins.

To make a quantitative comparison of thermal stability, heat-resistant index temperature ( $T_s$ , eq. (1))<sup>28</sup> is further employed to evaluate thermal stability of cured epoxy resin.

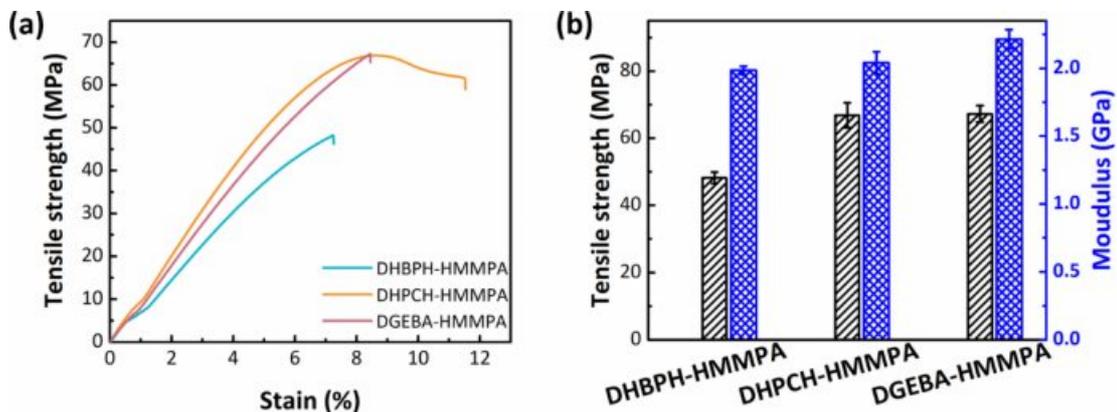
$$T_s = 0.49[T_{d,5\%} + 0.6(T_{d,30\%} - T_{d,5\%})] \quad (1)$$

where  $T_s$  is the statistic heat-resistant index temperature,  $T_{d,5\%}$  and  $T_{d,30\%}$  are the temperatures at 5% and 30% weight loss, respectively (Table 1). The calculated  $T_s$  values again demonstrate the best thermal stability of DHBPH-HMMPA among three cured epoxy resins.

**Dynamic Mechanical Properties of Different Cured Epoxy Networks.** Figure 6(a) and 6(b) show the dependence of storage modulus and  $\tan \delta$  of the cured epoxy resins on temperatures. It is observed one-step decrease of the storage modulus for all cured epoxy resins (Figure 6(a)). The values of storage modulus for DHBPH-HMMPA, DHPCH-HMMPA and DGEBA-HMMPA are 1.3, 1.9 and 1.4 GPa at room temperature, indicating that introduction of the bridge group with large size can evidently enlarge the rigidity of the cured resins. Moreover, Li *et al* reported that enlarging the size of the bridge group would lead to longer inter-segment distance, larger steric hindrance, worse chain movement and bigger storage modulus value,<sup>15</sup> which is consistent with the results observed in this



**Figure 6.** DMA curves of different cured epoxy resins: (a) storage modulus as a function of temperature; (b)  $\tan \delta$  as a function of temperature.



**Figure 7.** Tensile properties of three cured epoxy networks: (a) stress-strain curves of one of splines; (b) tensile strength and Young's modulus.

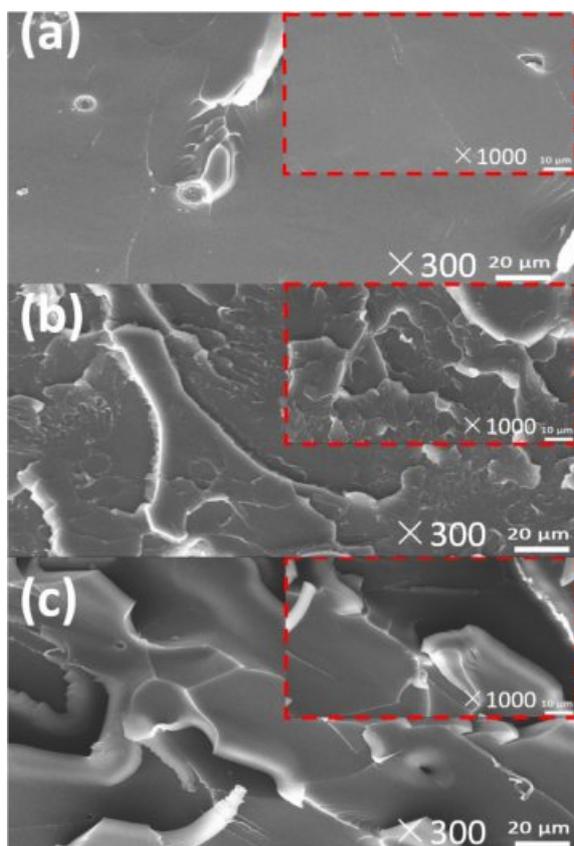
contribution.

The glass transition temperatures ( $T_g$ ) for three cured epoxy networks are determined by the peak temperatures of  $\tan \delta$  as a function of temperature (Figure 6(b)), which are 95.6, 136.6 and 145.6 °C, respectively. Obviously, the  $T_g$  values obtained from DMA are in good agreement with the results of DSC test. Again, one may notice that the cyclohexyl-bridged (DHPCH) and isopropyl-bridged (DGEBA) epoxy exhibited higher  $T_g$  values than that of single carbon-carbon bond bridged epoxy. This can also be ascribed to the motion resistance imparted by cyclohexyl and isopropyl groups to the crosslinked networks.

**Mechanical Properties of Different Cured Epoxy Networks.** The influences of the bridge groups on mechanical performances of cured epoxy resins were appraised by tensile properties of standard specimens (Figure 7).

Typical stress-strain curves for each cured epoxy resins are displayed in Figure 7(a), as it is shown, the DHPCH-HMMPA and DGEBA-HMMPA show higher tensile strength and larger

elongation at break than those of DHBPH-HMMPA. Moreover, the elongation at break value of DHPCH-HMMPA is larger than that of DGEBA-HMMPA, which is probably due to the fact the boat and chair conformation transformation of cyclohexyl group in DHBPH-HMMPA, and thus endow the DHBPH-HMMPA with more chain mobility.<sup>29</sup> Moreover, the higher tensile strength values of DHPCH-HMMPA and DGEBA-HMMPA than that of DHBPH-HMMPA is attributed to the fact that the bulky bridge group can increase the tensile strength of cured epoxy resin by restricting chain movement. It should be noted that the tensile strength of DHPCH-HMMPA and DGEBA-HMMPA are quite similar to each other, indicating the cyclohexyl and isopropyl may have the similar effects on enhancement of the tensile strength. When refer to the toughness of the DHPCH-HMMPA and DGEBA-HMMPA, the DHPCH-HMMPA exhibits more admired tensile toughness than that of DGEBA-HMMPA because of the deformation of the cyclohexyl ring.<sup>30</sup>



**Figure 8.** SEM images of tensile fracture of cured epoxy resins: (a) DHBPH-HMMPA; (b) DHPCH-HMMPA; (c) DGEBA-HMMPA.

The tensile strength and Young's modulus (average value) of three cured epoxy resins are shown in Figure 7(b). As expected, for epoxy resins containing bulky bridge groups (DHPCH-HMMPA and DGEBA-HMMPA) exhibit higher tensile strength and Young's modulus than those of the DHBPH-HMMPA. It is easy to conclude from the results of the mechanical tests that introducing bulky bridge group into the chemical structure of epoxy monomer is an efficient route to improve the mechanical properties of corresponding cured epoxy resin.

**Morphological Properties of the Different Cured Epoxy Networks.** Microscopic appearances of the fractured surfaces of three cured epoxy resins after the tensile testing were recorded by a SEM (Figure 8). As it is shown the epoxy bridged only with a single carbon-carbon bond (DHBPH-HMMPA) exhibits a smooth, glass-like, and very flat surface, which is the typical character of brittle fracture.<sup>31</sup> Comparatively, both the DHPCH-HMMPA and DGEBA-HMMPA demonstrate very rough fractured surfaces, suggesting better toughness than that of DHBPH-HMMPA. Since the chemical

structures of three epoxy monomers are very similar, it is reasonable to deduce that the bulky bridge groups in DHPCH and DGEBA are responsible for the increased toughness of the DHPCH-HMMPA and DGEBA-HMMPA. Moreover, the images obtained by SEM are also consistent with the results for the mechanical properties of the epoxy resins.

## Conclusions

Three model epoxy monomers (DHBPH, DHPCH and DGEBA) containing different bridge groups were carefully synthesized to evaluate the effects of bridge group on properties of cured epoxy resins. It is found the cured epoxy resins containing bulky bridge groups demonstrate higher  $T_g$  than the one only bridged with a single carbon-carbon bond. Moreover, the DMA and mechanical measurements demonstrate the bulky bridge groups can also endow the cured epoxy resins with admirable mechanical performances. The results presented in this contribution can be a meaningful guidance for establishing the relationship between the bridge group and the thermomechanical properties of corresponding cured epoxy resin.

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